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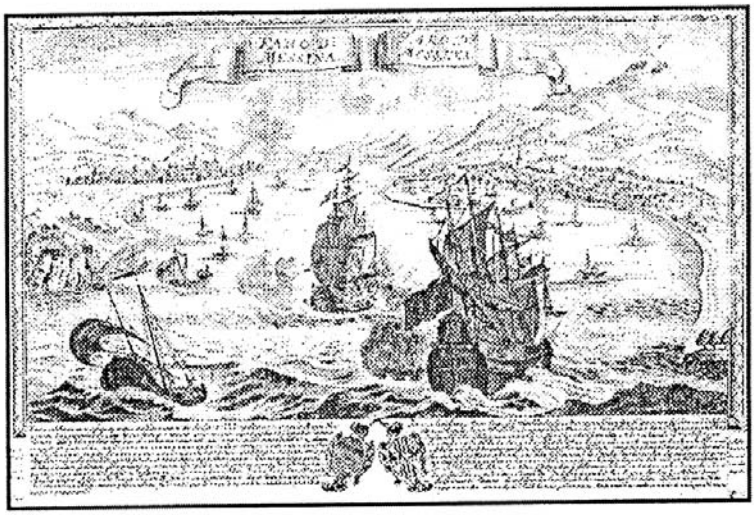
Atti Accademia Peloritana dei Pericolanti
Classe I di Scienze Fisiche
Matematiche e Naturali

WORKSHOP ON PLATINUM CHEMISTRY

ABSTRACTS



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NUCLEOPHILIC REACTIVITY: DISSECTION INTO STERIC AND ELECTRONIC CONTRIBUTIONS

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The sequence of the n°_{Pt} values in the scale of nucleophilic reactivity constants reflects roughly the characteristics of softness of the d^8 metal center.[1] There are, however, several severe deviations due to the π acceptor properties of the ligands and/or to electrostatic interactions. An additional limit comes from the fact that for a donor atom no account is taken of a steric contribution to the reactivity, even though steric effects can strongly influence the values of the derived parameters. For instance, the n°_{Pt} values listed for Ph_3P, nBu_3P and Et_3P are almost identical (8.93, 8.96, and 8.99, respectively) and can lead to the wrong conclusion that phosphines are all strongly reactive regardless of the nature of the substituents on the phosphorous atom.

We decided to obtain quantitative informations on the relative importance of steric and electronic factors in determining the reactivity of phosphines and amines toward platinum(II). To this purpose a model complex $[PtPh_2(CO)L]$ (L=5-aminoquinoline or SEt_2), was particularly designed to favour an associative

substitution. In addition: **i)** the complex is uncharged and soluble in nonpolar solvents **ii)** only one group (5-Aq or SEt_2) undergoes the substitution process **iii)** the lability of the leaving group is not too high or too low **iv)** the changes in the electronic spectra occur in the near visible region **v)** one of the coordinated ligands, CO in this case, is a good probe of the changes of electronic density or of the steric repulsions induced by the entering ligand *Y* in the reaction products *cis*-[$PtPh_2$(CO)(Y)].

The observed sequences of reactivity give the first extended scales of nucleophilic constants of phosphines[2] and amines[3] toward platinum(II). The values of the rate constants can be resolved quantitatively into electronic and steric effects, by means of correlations with the pKa values of the phosphines and amines or with some internal parameters of the system such as νCO, ^{1}J(PtP) or ^{1}J(PtCO) of the *cis*-[$PtPh_2$(CO)(Y)] products. The electronic profiles of the reactions show that the reactivity is only slightly affected by σ-inductive effects brought about by substituents on the phosphorus or nitrogen atoms while steric effects are dominant. Different shapes of steric profiles for the two reactions were obtained by correlating the reactivity data with different sets of steric parameters such as the ligand cone angles (θ) of space-filling CPK molecular models or the van der Waals steric repulsion (Er) as derived from molecular mechanics calculations. Limits and significance of such relationships are discussed in order to account for apparently conflicting interpretations.

For the most sterically hindered amines, such as $NHCy_2$ or NEt_3, the bimolecular attack is prevented and the reaction proceeds only by way of a nucleophile independent pathway, which most likely involves dissociation of a ligand (5-Aq or SEt_2) from the coordination sphere of the metal. The same pathway controls the reaction with nitrogen bidentate ligands N-N, such as 2,2'-bipyridine or 1,10-phenanthroline, to yield [$PtPh_2$(N-N)], where a fast ring closure follows the

displacement of 5-Aq or SEt_2. In contrast, in the reactions with 1,2-diaminoethane, 1,3-diaminopropane, 2-aminomethylpyridine, 2-aminoethylpyridine, 2,2'-dipyridylamine it is possible to observe by ^1H NMR the formation of an intermediate open-ring $[PtPh_2(CO)N\text{-}N]$ species, which eventually interconverts slowly into the final $[PtPh_2(N\text{-}N)]$ product. The proper kinetics were followed by IR or ^1H NMR spectroscopy. The contemporary presence in the starting substrate of a labile (SEt_2) and a relatively inert (CO) ligand allows for the isolation of some stable open ring species such as that obtained with N-phenyl-1,2-diaminoethane, where the two nitrogen atoms exhibit widely different basicity and steric hindrance. Preliminary results with hybrid bidentate ligands of the type P-N and P-S showed a fast entry of the phosphorus end of the molecule followed by a relatively slow ring closure.

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